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Poly(ionic liquid) assisted synthesis of hierarchical gold-platinum alloy nanodendrites with high electrocatalytic properties for ethylene glycol oxidation and oxygen reduction reactions

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ABSTRACT

Herein, a facile one-pot method is developed to prepare three-dimensional (3D) hierarchical AuPt alloy nanodendrites (AuPt NDs) with the assistance of poly(ionic liquid) as the green shape-regulator and stabilizer. The as-synthesized architectures show enlarged electrochemically active surface area, and enhanced maximum mass activity (3616 mA mg^{-1}) for ethylene glycol oxidation reaction (EGOR) in alkaline media. Furthermore, the as-synthesized AuPt NDs exhibit superior catalytic activity and more positive onset potential (0.89 V *vs.* RHE) toward oxygen reduction reaction (ORR) in 0.1 M $HClO_4$ via the four-electron pathway, owing to the unique nanostructures as well as the synergistic effects between Au and Pt.

Introduction

Ionic liquids (ILs) are organic salts with low-melting points near or below room temperature, which have drawn significant research interest recently, owing to their interesting and unique physicochemical properties such as high ion conductivity, good chemical and thermal stability, strong dissolving ability and solvent miscibility [1–4]. Polymeric ILs [poly(ILs)] are obtained by polymerizing the ionic liquid monomers, resulting in smart control over their unique physicochemical properties in association with the advantages of polymers-stability and durability [5–7]. Based on their unique properties, ILs and poly(ILs) are widely applied for the synthesis of multi-structural nanomaterials [8].

Up to now, many inorganic nanocomposites with various morphologies were prepared with the assistance of ILs. Xie's group synthesized triangle and hexagon polyhedron gold nanosheets in the presence of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) [9]. Similarly, Wang and Yang

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fabricated CoPt nanorods in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf_2N]) with the help of cetyltrimethylammonium bromide (CTAB) [10]. Hierarchical, three-fold symmetrical Au nanodendrites were also obtained by using ionic liquid ([BMIM][PF_6]) [11].

Noble metal nanomaterials with intriguing morphology were extensively investigated, thanks to their fundamental scientific interest and potential applications in fuel cells to solve the energy crisis and environmental pollution [12,13]. For example, Sun's group prepared tetrahexahedral Pt nanocrystals with enhanced electrocatalytic activity towards formic acid and ethanol oxidation when compared with spherical Pt nanoparticles [14]. Xu and coworkers constructed Pt–Cu nanocubes with superior catalytic activity for methanol oxidation [15]. Zheng et al. prepared reduced graphene oxide supported popcorn-like PtAu nanocrystals, which displayed improved catalytic activity towards methanol oxidation as compared to commercial Pt–C catalyst [16].

Polyhydric alcohol especially ethylene glycol is the most promising alternative fuel in direct alcohol fuel cells, because of its lower toxicity and volatility, along with higher energy density than methanol [17,18]. In addition, ethylene glycol can be easily electrochemically oxidized, and show the higher reactivity than methanol and other polyhydric alcohols in alkaline media [19].

Pt nanomaterials are proved to be the most effective catalysts in fuel cells [20], while their reliability and cost are the major obstacles for their commercial applications in fuel cells [21]. Combining Pt with other metals (such as Pd and Au) can greatly improve the catalytic performances of Pt-based nanocatalysts [22]. Among them, Au is the most attractive second metal because of its more electro-negativity than Pt counterpart [23]. The electronic state of Pt would be modified by alloying with Au, leading to the enhanced electrocatalytic activity and durability [24,25]. For example, Liu's group found that the incorporation of Au would reduce the *in situ* O coverage and thereby protect the neighboring Pt active sites from corrosion in oxygen reduction reaction (ORR) [26].

Herein, we report a facile route for the preparation of three-dimensional (3D) hierarchical $Au_{75}Pt_{25}$ alloyed nanodendrites ($Au_{75}Pt_{25}$ NDs) in the presence of poly(ionic liquid) (poly(1-vinyl-3-ethylimidazolium bromide), poly(ViEtImBr), Fig. S1, Electronic Supplementary Information, ESI) as the green shape-regulator and stabilizer. Moreover, the hybrid nanocrystals exhibit an enhanced catalytic activity towards ethylene glycol oxidation reaction (EGOR) and oxygen reduction reaction (ORR).

Experimental

Synthesis of 3D hierarchical AuPt alloy nanodendrites

The typical synthesis of $Au_{75}Pt_{25}$ NDs was carried out as following. Firstly, 823 μL of $HAuCl_4$ (24.30 mM) and 518 μL of H_2PtCl_6 (38.62 mM) were dissolved into 10 mL of 0.2% poly(-ViEtImBr) aqueous solution to obtain a homogeneous suspension under stirring, in which the final molar ratio of $HAuCl_4$ to H_2PtCl_6 was 1:1. Secondly, the freshly prepared ascorbic acid solution (AA, 1 mL, 0.1 M) were drop-wised put

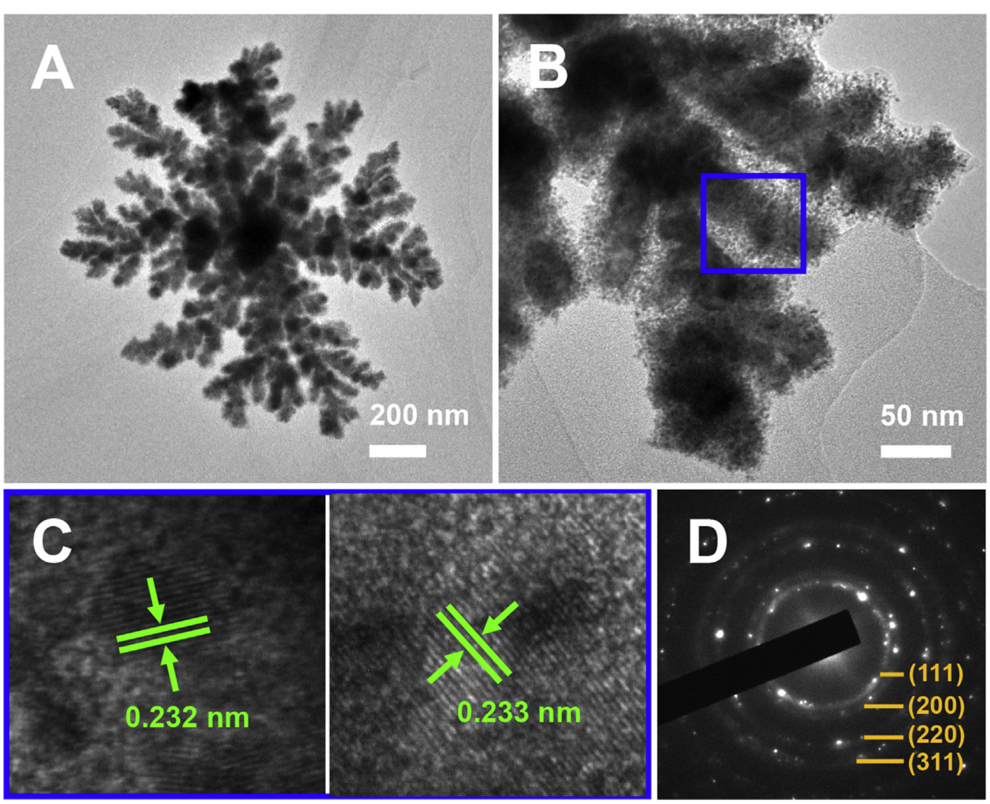

Fig. 1 – (A–B) TEM and (C) HR-TEM images of $Au_{75}Pt_{25}$ NDs. (D) The corresponding SAED pattern.